

# (12) UK Patent Application (19) GB (11) 2 302 824 (13) A

(43) Date of Publication 05.02.1997

(21) Application No 9613548.8

(22) Date of Filing 27.06.1996

(30) Priority Data

(31) 9507978

(32) 29.06.1995

(33) FR

(71) Applicant(s)

Institut Francais du Petrole

(Incorporated in France)

4 Avenue de Bois-Preau, 92502 Rueil-Malmaison,  
France

(72) Inventor(s)

Jean Morlec

Christian Hamon

(74) Agent and/or Address for Service

D Young & Co

21 New Fetter Lane, LONDON, EC4A 1DA,  
United Kingdom

(51) INT CL<sup>6</sup>

B01J 20/18

(52) UK CL (Edition O )

B1L LAE L208 L308 L602X

U1S S1279 S1280

(56) Documents Cited

EP 0224150 A

US 4447353 A

WPI Abstract 95-182187/24 & JP070100327A WPI

Abstract 95-027348/04 & JP060312132A WPI Abstract

89-210714/29 & JP010148341A WPI Abstract

87-039070/06 & JP610293548A WPI Abstract

85-226784/37 & JP600147240A

(58) Field of Search

UK CL (Edition O ) B1L LAE

INT CL<sup>6</sup> B01J 20/18

ONLINE: WPI

(54) Adsorbents for use in processes for purifying gases

(57) An adsorbent comprising at least one zeolite and at least one metallic cation selected from Ag<sup>+</sup> and Cu<sup>2+</sup> is used in a process for purifying atmospheres containing traces of various pollutants, e.g. ethylene. The zeolite may be zeolite-Y or mordenite.

GB 2 302 824 A

**ADSORBENTS FOR USE IN PROCESSES FOR PURIFYING**  
**ATMOSPHERES POLLUTED WITH ETHYLENE**

The present invention concerns an adsorbent comprising at least one zeolite and at least one metallic cation selected from the group formed by copper ( $\text{Cu}^{2+}$ ) and silver ( $\text{Ag}^+$ ).

- 5           The invention also concerns a process for purifying atmospheres containing traces of various pollutants, using the adsorbent.

Polluted atmospheres of this type can contain pollutants, for example ethylene, in a concentration in the range 10 ppb to 10000 ppb, or even between 10 ppb and 1000 ppb.

- 10           Charcoal is sometimes used as an adsorbent. However, it cannot effectively absorb ethylene when present in low concentrations. The advantage of zeolites over charcoal for this type of application is due to the attraction of their rectangular isotherms which mean that non negligible adsorption capacities can be achieved at low partial pressures.

- 15           Ethylene is known to be adsorbed by zeolite. However, when the ethylene concentration is low, zeolites alone are no longer satisfactory. The development of novel adsorbents which are effective even at low ethylene concentrations is therefore of importance.

- 20           Some fruit and vegetables generate ethylene, for example cauliflowers, artichokes and certain flowers. This ethylene, which can accumulate in ripening depots, storage facilities or transport trucks for example, cause premature ripening even at low concentrations (several ppm) and are thus prejudicial to preserving these fruit and vegetables. It is thus necessary to have access to an adsorbent which can fix the ethylene present, even at low concentrations.

- 25           Our research has led to the surprising discovery that an adsorbent containing at least one zeolite into which at least one metallic cation selected from

the group formed by  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  has been incorporated can adsorb ethylene present in low concentrations in the atmosphere.

Different types of zeolites are suitable for this application, in particular Y type zeolites and mordenite type zeolites.

5 Since industrial gas for treatment sometimes contains water vapour, nitric acid can form on the zeolite. It is sometimes preferable in this case to use products which are stable to an acid medium, i.e., the acid form of zeolites. Occasionally, it is also preferable to use zeolites with a hydrophobic nature, and hence a relatively high Si/Al ratio, for example in the range 10 to 40, to limit  
10 water adsorption which would be deleterious to the efficiency of the process as regards the level of adsorption of target molecules and possible regeneration of the adsorbent.

The adsorbent of the invention thus comprises at least one zeolite into which at least one metallic cation selected from the group formed by  $\text{Ag}^+$  and  
15  $\text{Cu}^{2+}$  has been incorporated. The choice of cation and zeolite and the cation concentration has an important effect on the ethylene retention efficiency, as will be shown in the examples below.

These cations are incorporated using known methods for introducing metals into zeolites, namely exchange or impregnation. The general conditions  
20 for incorporation are as follows:

Salt	:	Nitrate or acetate
Concentration	:	3M
Temperature	:	60°C
Duration	:	5 hours

25 The percentages are analysed using inductively-coupled plasma atomic spectroscopy (ICP).

The ion exchange capacity of the zeolite reduces as the Si/Al ratio increases.

The concentration of exchanged or impregnated cation is in the range 0.01% to 10%, preferably in the range 0.1% to 10%, more preferably in the range 2% to 10%.

The adsorbents of the invention can be used in processes for purifying atmospheres containing various pollutants.

These processes comprise an adsorption phase, which may be associated with a regeneration phase which, depending on the method used, can be successive or continuous.

When using a fixed bed method, the two phases are successive: firstly, the reactor is used for adsorption, then when the adsorbent is saturated, the same reactor enters a regeneration phase.

Continuous regeneration of the adsorbent is an alternative method. The bed of adsorbent is thus mobile, the adsorbent passing successively from the adsorption reactor to the regeneration reactor then again to the adsorption reactor and so on, meaning continuous injection of regenerated adsorbent.

Whatever the method used, the atmosphere to be treated in the adsorption reactors contains a pollutant, for example ethylene, in a concentration in the range 10 ppb to 10000 ppb. The adsorbent is also effective at lower pollutant levels, for example in the range 10 ppb to 1000 ppb.

The adsorbent used in these purification processes is that of the invention: it comprises at least one zeolite into which at least one metallic cation selected from the group formed by  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  has been incorporated. The zeolite is, for example, a Y type zeolite or a mordenite type zeolite, it can optionally be in its acid form and it may have a Si/Al ratio in the range 10 to 40.

The purification process can also be carried out after dehumidification using a known technique, for example using a hydrophobic type 4A zeolite.

The following examples illustrate the invention without limiting its scope.

### PRINCIPLE

5 In these examples, dynamic adsorption is carried out using a fixed bed of zeolite.

The tests were carried out under the following general conditions:

- 2 cm<sup>3</sup> microreactor - diameter: 5.5 mm; Length: 84 mm;
- granulometry of adsorbent: 0.5 < diameter < 1 mm;
- 10 • relative humidity: variable depending on examples;
- HSV: 10000 h<sup>-1</sup>;
- ethylene concentration: 5 ppm

The gas mixture was prepared from a calibrated mixing bottle containing 51.3 ppm of C<sub>2</sub>H<sub>4</sub> in nitrogen, diluted with air to adjust the concentration to 5  
15 ppm.

The ethylene concentration was analysed using GC.

The tests used different types of zeolites (Y or mordenite) into which at least one cation Ag<sup>+</sup> or Cu<sup>2+</sup> had been incorporated. Incorporation was effected using exchange or impregnation under the following general conditions:

20	Salt	:	Nitrate or acetate
	Concentration	:	3M
	Temperature	:	60°C
	Duration	:	5 hours

25

### EXAMPLE 1

These tests were carried out under the following conditions:

ethylene concentration : 5 ppm

relative humidity : <1% at 20°C.

They were carried out on different adsorbents whose characteristics are shown in Table 1 below, along with the results.

5

TABLE 1

Test	Zeolite	Si/Al	Exchange or impregnation	Cation	% mass cation	Adsorb (g)	Time to leakage	Capacity/ unit mass (mg/g)
A1	Y	40	e	Ag	6.96	1.479	27h40mn	1625
B1	Y	100	i	Ag	0.8	1.009	4h	289
C1	mord	10	e	Ag	5.81	1.759	45h50mn	1973
D1	mord	37	e	Ag	3.29	1.638	24h45mn	672
E1	Y	40	e	Cu	1.85	1.307	20mn	48
F1	Nay	3	e	Cu	6.99	1.601	3h20mn	149
G1	mord	6	e	Cu	4.2	1.184	1h30mn	44

The results are conclusive: zeolites with at least one  $Ag^+$  or  $Cu^{2+}$  cation incorporated therein formed efficient adsorbents and were more efficient when the cation was  $Ag^+$  (higher time to leakage and capacity/unit mass).

Efficiency increased with cation concentration.

10

### EXAMPLE 2

The tests were carried out under the following conditions:

ethylene concentration : 5 ppm

relative humidity : 70% at 20°C.

The characteristics of the adsorbents used and the results obtained are

15

shown in Table 2 below.

TABLE 2

Test	Zeolite	Si/Al	Exchange or impregnation	Cation	% mass cation	Adsorb (g)	Time to leakage	Capacity/ unit mass (mg/g)
A2	Y	40	e	Ag	6.96	1.5	25	23
D2	mord	37	e	Ag	3.29	1.63	15	10
H2	Y	100	i	Ag	2	1.3	5	5
E2	Y	40	e	Cu	1.85	1.3	15	18
F2	Nay	3	e	Cu	6.99	1.4	35	48

The adsorbents were less effective under these conditions than under the previous conditions, however, the  $H_2O$ /ethylene concentration ratios in the atmosphere were very high.

### EXAMPLE 3

5 This test was conducted at lower humidity: 30% at  $20^\circ C$ .

The efficiency increased with respect to the previous test.

TABLE 3

10

Test	Zeolite	Si/Al	Exchange or impregnation	Cation	% mass cation	Adsorb (g)	Time to leakage	Capacity/unit mass (mg/g)
H3	Y	100	i	Ag	2	1.25	25	18

15 These tests showed that adsorbents comprising at least one zeolite into which at least one cation selected from the group formed by  $Cu^{2+}$  and  $Ag^+$  were effective in adsorbing low concentrations of ethylene in air, in particular in the absence of humidity.

**CLAIMS**

1. An adsorbent comprising at least one zeolite into which at least one metallic cation selected from the group formed by  $\text{Ag}^{2+}$  and  $\text{Cu}^{2+}$  has been incorporated.  
5
2. An adsorbent according to claim 1, in which said at least one zeolite is selected from the group formed by Y type zeolite and mordenite type zeolite.  
10
3. An adsorbent according to claim 1 or claim 2, comprising at least one zeolite in its acid form.
4. An adsorbent according to any one of claims 1 to 3, comprising at least one zeolite with a Si/Al ratio in the range 10 to 40.  
15
5. An adsorbent according to any one of claims 1 to 4, in which at least one metallic cation is  $\text{Ag}^+$ .
- 20 6. An adsorbent according to any one of claims 1 to 5, in which the cation concentration is in the range 0.01% to 10%.
7. An adsorbent according to any one of claims 1 to 6, in which the cation concentration is in the range 0.1% to 10%.
- 25 8. An adsorbent according to any one of claims 1 to 7, in which the cation concentration is in the range 2% to 10%.



5 9. A process for the purification of polluted atmospheres, comprising an adsorption phase, during which an adsorbent is used which comprises at least one zeolite into which at least one metallic cation selected from the group formed by  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  has been incorporated.

10 10. A process according to claim 9, in which the atmosphere to be purified contains at least one pollutant in a concentration in the range 10 ppb to 10000 ppb.

11. A process according to claim 9 or claim 10, in which the pollutant concentration is in the range 10 ppb to 1000 ppb.

12. A process according to any one of claims 9 to 11, in which at least one pollutant is ethylene.

13. A process according to any one of claims 9 to 12, in which the cation concentration is in the range 0.01% to 10%.

20 14. A process according to any one of claims 9 to 13, in which said at least one cation is  $\text{Ag}^+$ .

15. A process according to any one of claims 9 to 14, in which the cation concentration is in the range 0.1% to 10%.

25 16. A process according to any one of claims 9 to 15, in which the cation concentration is in the range 2% to 10%.

17. A process according to any one of claims 9 to 16, in which the adsorption phase is associated with a regeneration phase.
- 5 18. A process according to claim 17, in which the adsorption and regeneration phases take place successively in the same reactor.
19. A process according to claim 17, in which the adsorption and regeneration phases take place continuously, the adsorbent circulating from a reactor in adsorbing mode to a reactor in regeneration mode.
- 10



Application No: GB 9613548.8  
Claims searched: 1-19

Examiner: C.A. Clarke  
Date of search: 7 October 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B1L (LAE)

Int Cl (Ed.6): B01J 20/18

Other: ONLINE : WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0224150 A NIPPON KOKAN see whole document	1-4,6-11 at least
X	US 4447353 US DEPT of ENERGY see claim 1	1-11 at least
X	Derwent Abstract 95-182187/24 & JP 070100327A	1-11 at least
X	Derwent Abstract 95-027348/04 & JP 060312132A	1-11 at least
X	Derwent Abstract 89-210714/29 & JP 010148341A	1, 3-16 at least
X	Derwent Abstract 87-039070/06 & JP 610293548A	1-11 at least
X	Derwent Abstract 85-226784/37 & JP 600147240A	1-16 at least

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

